

NONADIABATIC PHOTO-PROCESS INVOLVING THE  $\pi\sigma^*$  STATE IN INTRAMOLECULAR CHARGE TRANSFER: A CONCERTED SPECTROSCOPIC AND COMPUTATIONAL STUDY ON 4-(DIMETHYLAMINO)BENZETHYNE AND 4-(DIMETHYLAMINO)BENZONITRILE.

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The ubiquitous nature of the low-lying  $\pi\sigma^*$  state in the photo-excited aromatic molecules or biomolecules is widely recognized to play an important role in nonadiabatic photo-process such as photodissociation or intramolecular charge transfer (ICT). For instance, the O–H elimination channel in phenol is attributed to the state-cross of the repulsive  $\pi\sigma^*$  state that exhibits a conical intersection with the lowest bright  $\pi\pi^*$  state and with the ground state, leading to ultrafast electronic deactivation. A similar decay pathway has been found in the ICT formation of 4-(dialkylamino)benzonitriles in a polar environment, where an initially photoexcited Frank-Condon state bifurcates in the presence of a dark intermediate  $\pi\sigma^*$  state that crosses the fluorescent  $\pi\pi^*$  state, followed by a conical intersection with the twisted intramolecular charge transfer (TICT) state. We proposed such a two-fold decay mechanism that  $\pi\sigma^*$ -state highly mediates intramolecular charge transfer in 4-(dialkylamino)benzonitriles, which is supported from both our high-level *ab initio* calculations and ultrafast laser spectroscopies in the previous study.

4-(Dimethylamino)benzethyne (DMABE) is isoelectronic with 4-(dimethylamino)benzonitrile (DMABN), and the electronic structures and electronic spectra of the two molecules bear very close resemblance. However, DMABN does show the ICT formation in a polar environment, whereas DMABE does not. To probe the photophysical differences among the low-lying excited-state configurations, we performed concerted time-resolved laser spectroscopies and high level *ab initio* multireference perturbation theory quantum-chemical (CASPT2//CASSCF) computations on the two molecules. In this paper we demonstrate the importance of the bound excited-state of a  $\pi\sigma^*$  configuration that induce highly  $\pi\sigma^*$ -state mediated intramolecular charge transfer in 4-(dialkylamino)benzonitriles.